Cyclic Voltammetry and in situ Infrared Reflection Absorption Spectroscopy on Kinetic Effect of Physisorbed Dioctadecylsulphide on a Cu-UPD Process on Au(111) Electrode Surface*

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The presence of a self-assembled monolayer (SAM) of dioctadecyl sulphide (DOS) on a Au(111) electrode affects the underpotential deposition (UPD) of copper in sulfuric acid solution. The first stage of the UPD, i.e., formation of the $\sqrt{3}\times\sqrt{3}$ R30° lattice comprising the honeycomb structure of copper, is delayed by the DOS SAM of the lower-density phase, in which the chain axis is parallel to the surface. Neutral molecules are preferentially adsorbed on the Au(111) electrode surface at around the potential of zero charge (pzc), which is approximately −0.1 V (vs. Hg/HgSO₄) in sulfuric acid solution. The adsorption of copper ions at this potential is inhibited by the DOS SAM, which delays the successive Cu-UPD process in the first stage. In contrast, the DOS SAM of the higher-density phase, in which the chain axis is standing upright, inhibits the entire UPD process. [DOI: 10.1380/ejssnt.2018.60] Keywords: Alkyl sulphide; Au(111); Self-assembled monolayer; IRAS

I. INTRODUCTION

A self-assembled monolayer (SAM) of chain molecules on a solid surface is an important system in the field of surface and interface science because of its widespread applications such as surface functionalization [1], corrosion prevention [2], surface patterning [3], and stabilization of nanoclusters and nanoparticles [4]. The most common SAMs comprise alkanethiol molecules on a Au(111) surface, in which the terminal-SH bond is cleaved and the sulfur atom forms chemical bonds with the substrate Au atoms. Owing to bond formation, the gold surface becomes completely “invisible” from the outside because of the shield of alkyl chains, which is standing upright. Therefore, the functionality of the SAM is expressed only through the head groups exposed to the outer surface.

In contrast, long alkyl chains adsorbed on inert surfaces such as a graphite basal plane and Au(111) surface are flat-lying and form a self-assembled lamellar structure [5–11]. The SAMs of these lamellar structures are expected to show a different class of functionalities. Because the chain is flat-lying, functional groups can be arranged at any location within the molecules, other than the terminal or head positions, and is exposed and accessible. The van der Waals interactions among the molecules and substrate play important roles in the assembly and make the SAM structures flexible. Owing to the low-dimensional nature, the lamellae provide an ideal substrate for constructing one- or two-dimensional nanostructures on the molecular scale [11].

The characteristics of the SAMs of flat-lying molecules are highlighted by comparing the structure and functionality with those of the SAMs of the standing molecules. The SAMs of two structures comprising the same molecules are suitable samples to elucidate such a difference clearly. For this purpose, dioctadecylsulphide (DOS) is an ideal choice of molecule, which forms a lamellar structure at low densities and a densely packed triangular lattice at high densities on the Au(111) surface [12, 13]. The chain is flat-lying on the former structure, and upright standing on the latter. Because the sulfur atom is connected to the carbon atoms on both sides, the −CSC− bond cleavage does not occur upon adsorption and the molecules remain intact [14–16]. Therefore, the S–Au interaction is not very strong compared to the SAM of thiols, which affects the kinetic process of SAM formation [17]. As a result, the SAM with the flat-lying sulphide chains can be more easily obtained than the thiol. Although the SAM of sulphide is less extensively studied compared with the SAM of thiol, the sulphide is attracting much interest lately as a SAM constituent [18].

Behavior of the SAM in the electrolyte solution and its response to the applied potential are important for exploiting its function as a modified electrode. The process concerning the SAM functionalities such as the molecular recognition, surface catalytic reaction, corrosion prevention, and metal deposition is related to the electrochemical reactions that occur through the SAM. Therefore, the effect of the SAM on electron transfer and ion adsorption at the electrochemical interface is crucial to comprehend the SAM functions. Although the electrochemical stability of thiol SAM in a certain potential range has been reported [19], little is known about the sulphide SAM.

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In this study, we have investigated the effect of DOS SAMs on Au(111) on the underpotential deposition (UPD) of copper in a sulfuric acid solution. The UPD is the heteroepitaxial deposition of metal, which occurs at a more positive potential than the equilibrium (Nernst) potential and is regarded as the first stage of metal electropolating. Therefore, the UPD is not only scientifically interesting but also technologically important for the decollation of the surface of metals, including nanoparticles [20, 21]. Because most nanoparticles are stabilized with SAMs, the study and knowledge of the effect of SAMs on the UPD process are indispensable. The Cu-UPD on Au(111) in sulfuric acid solution is one of the most extensively studied UPD systems by many electrochemical and surface science techniques [22–28]. In this study, the electrochemical process is monitored by cyclic voltammetry (CV) based on the molecular density of the SAMs. The change in the molecular orientation and adsorption of the (bi)sulfate anion is observed by in situ infrared reflection absorption spectroscopy (IRAS).

II. EXPERIMENTAL

A polished single crystal of Au(111) (MaTeCk, GmbH, Germany) was used as the electrode. The DOS SAMs were prepared either from n-hexane solution, or by vapor deposition. The substrate was cleaned by H2 flame annealing and cooled under a nitrogen atmosphere for solution preparation. The DOS (> 96.0% (GC), Tokyo Chemical Industry Co. Ltd., Japan) was dissolved in n-hexane solution (super pure grade, KOKUSAN CHEMICAL Co., Ltd., Japan). The concentration was ca. 0.5 mM. The cleaned surface was immersed in the solution for 2 s or 24 h and rinsed with pure n-hexane. All the CVs and in situ IRAS measurements were conducted in 1 mM CuSO4 (super pure grade, KOKUSAN CHEMICAL Co., Ltd., Japan) + 0.05 M H2SO4 (Super Special Grade, Wako Pure Chemical Industries, Ltd., Japan), prepared with Milli-Q water (18.2 MΩ). Vapor deposition was performed under ultrahigh vacuum (UHV) (base pressure: 1 × 10^-7 Pa) at room temperature on the Au(111) surface, which was precleared by a repeated cycle of Ar+ sputter (1.5 kV) and annealing (800 K). The DOS in powder form contained in a glass tube was evaporated by resistive heating. The adsorption amount was checked with a thickness monitor. The thickness corresponds to a monolayer of flat-lying chain molecules is estimated as 5 Å by observing the n-alkane monolayer [29]. The Au(111) surface covered with the DOS SAM was transferred to a conventional electrochemical cell equipped with a Pt counter electrode and a Hg|Hg2SO4 reference electrode. The quality of the Au(111) electrode was confirmed by the CV of the Au(111) electrode in the 0.5 M H2SO4 solution as shown in Fig. 1(a), which exhibits a typical shape [30]. After the CV measurement, the Au(111) surface covered with the DOS SAM is emersed from the solution at pzc and is transferred to a Teflon-body electrochemical cell for the IRAS measurement, equipped with a Pt counter electrode and a Hg|Hg2SO4 reference electrode. In situ IRAS analyses were conducted using an FT-IR 4700 instrument (JASCO International Co., Ltd.) equipped with a mercury cadmium telluride (MCT) detector. A CaF2 crystal was placed on the window. The incident angle of the IR radiation polarized along the surface normal direction was ca. 70°.

III. RESULTS AND DISCUSSIONS

Figure 1(b) shows the cyclic voltammograms (CVs) of the DOS-modified and bare Au(111) electrode in the 1 mM CuSO4 + 0.05 M H2SO4 solution, which were measured at a sweep rate of 50 mV/s. The black line shows the CV of the bare Au(111) electrode, which exhibits two pairs of peaks labeled as peak I, I' and II, II'. The first stage of the Cu-UPD involves the formation of the √3 × √3 lattice of the honeycomb structure of the 2/3 monolayer (ML) of copper coadsorbed with the 1/3 ML of (bi)sulfate, which occurs through peak I [22–28]. The second stage, related to peak II, corresponds to the additional adsorption of 1/3 ML of copper to form the 1 × 1 structure [22–28]. The green line shows the CV of the Au(111) electrode covered with the DOS SAM, which was prepared by immersing the bare Au(111) electrode for 24 h in the DOS solution. The SAM obtained by such a long immersion comprises DOS molecules with the upright-standing orientation in a higher-density phase [12, 13].
FIG. 2. Sweep-rate-dependent CVs for (a) DOS-modified and (b) bare Au(111) electrodes in 1 mM CuSO$_4$ + 0.05 M H$_2$SO$_4$ solution.

FIG. 3. Peak potentials of CVs in Fig. 2 as a function of the square root of sweep rate. (a) DOS-modified and (b) bare Au(111) electrodes in 1 mM CuSO$_4$ + 0.05 M H$_2$SO$_4$ solution.

No current flows in the entire potential region; hence, the Cu-UPD does not occur on this electrode. In contrast, the Au(111) electrode with the DOS SAM obtained by a short immersion time (2 s), which corresponds to the SAM consisting of flat-lying molecules in a low-density phase [12, 13], shows the CV as a red line. Peak I is not observed in this CV, which is related to the first stage of the Cu-UPD; hence, the process is somehow affected by the DOS SAM, although the other processes are not much influenced.

The disappearance of peak I for the Au(111) electrode modified with the DOS SAM with a low-density phase is discussed with the CVs obtained by slower sweep rates (1, 2, 5, and 10 mV/s), which are shown in Fig. 2. The DOS monolayer was prepared by vapor deposition for these CV measurements, and it exhibits the same CV as that obtained for the DOS monolayer prepared by 2 s immersion into the DOS solution. The DOS layers obtained by the vapor deposition exhibit the same CVs up to the thickness of 8 Å (nominally 1.6 ML). For the DOS layer with a density more than 2 ML, peak II is considerably quenched (not shown). Therefore, the monolayer prepared from the solution with a short immersion time is comprising the layer with a thickness of less than 2 ML. The peaks labeled as peak I are observed as broad bands in these CVs in Fig. 2(a) at considerably negative potentials compared with peaks I for the bare Au(111) electrode shown in Fig. 2(b). Therefore, the UPD process related to peak I is not completely missing but is delayed. The charging current is not observed at the potentials more positive than peak I. This is clearly shown by comparing the CVs of the bare Au(111) electrode shown in Fig. 2(b). The charging current at this potential region is attributed to the random adsorption of copper cations and desorption or re-adsorption of some (bi)sulfate anions [27]; hence, the DOS SAM inhibits the adsorption of copper and (bi)sulfate ions at the initial stage of the Cu-UPD process.

Figure 3 shows the peak potentials as a function of the square root of the sweep rate for the DOS SAM-modified (a) and bare (b) Au(111) electrodes. Peaks I', II, and II' exhibit almost the same tendency for both the electrodes. Therefore, the processes concerning these peaks are not much affected by the DOS SAM. The linear relation between the peak potential and the square root of the sweep rate is attributed to an instantaneous nucleation and growth process [28]. In contrast, the plot of peak I for the DOS-modified electrode deviates considerably from the plot of peak I for the bare Au(111) electrode. The peak potentials shift to a more negative value as the
For stage one of the Cu-UPD process, i.e., formation of peak I', this indicates the appearance of hysteresis. The potentials of this hysteresis region, the in situ points are almost the same for both peak I and peak I'.

To elucidate what occurs at the electrode interface at the potentials of this hysteresis region, the in situ IRA spectra were measured. Figure 4 shows the IRA spectra of the Au(111) electrode covered with the DOS SAM in the 1 mM CuSO$_4$ + 0.05 M H$_2$SO$_4$ solution. The wavenumber regions of the CH-stretching vibrational mode (a) and the SO-stretching vibrational mode (b) are displayed. The bands observed in the CH-stretching vibrational mode region are assigned to the SO$_3$-symmetric stretching mode of the (bi)sulfate anion. The wavenumber of ca. 1225 cm$^{-1}$ at the peaks corresponds to the (bi)sulfate on the Cu-UPD layer [32]. Therefore, these bands indicate the formation of the Cu-UPD layer on the Au(111) electrode.

Figure 5 shows a schematic of the interfacial structures based on the potentials in the Cu-UPD region. At the positive potentials, the Au(111) surface is completely covered with the DOS molecules with the flat-on orientation. The SAM inhibits the adsorption of copper and (bi)sulfate ions on the surface; as a result, no charging current flows. This is caused by the strong interactions between the neutral DOS molecules and the Au(111) surface at the potential of zero charge (pzc), which is estimated at approximately $-0.1$ V [27]. Because the alkyl chains are hydrophobic, they are forced out of the water phase and adsorbed on the Au(111) surface. It is generally accepted that the neutral molecules are preferentially adsorbed on the surface at potentials around the pzc [33–35]. The large adsorption energy of the DOS molecules may surpass the adsorption energy of Cu cations in the random adsorption region, though it is difficult to estimate and compare the adsorption energy at an electrolyzed interface. Owing to the inhibition of copper adsorption, the formation of the $\sqrt{3} \times \sqrt{3}$ structure is delayed until a certain amount of Cu cation is adsorbed on the surface by applying a more negative overpotential. This is why peak I, which corresponds to the formation of the $\sqrt{3} \times \sqrt{3}$ phase, is shifted to a more negative potential for the DOS-modified Au(111) electrode. Ion adsorption is preferred because of the strong electrostatic interactions at sufficiently negative potentials; therefore, the DOS molecules are exchanged with copper and (bi)sulfate ions at a more negative potential and the Cu-UPD layer is formed. Once the Cu-UPD layer is formed, it covers the Au(111) electrode surface in the same potential region as the bare Au(111) electrode, which is suggested by the occurrence of peak I' at almost the same potential as observed for the bare Au(111) electrode. However, the charging current is almost undetectable at potentials more positive than peak I'; hence, the Cu cations and (bi)sulfate anions are com-

![Figure 4](https://www.jstage.jst.go.jp/browse/ejssnt/63)

**FIG. 4.** (a) CH- and (b) SO-stretching vibration region of in situ IRA spectra for DOS-modified Au(111) electrode in 1 mM CuSO$_4$ + 0.05 M H$_2$SO$_4$ solution. (c) CV for indicating reference and measurement potentials, obtained by 50 mV/s.

The extrapolated point to the zero sweep rate for peak I does not coincide with the point for peak I'. This indicates the appearance of hysteresis for stage one of the Cu-UPD process, i.e., formation of a $\sqrt{3} \times \sqrt{3}$ structure. This is not the case for the bare Au(111) electrode because the values of the extrapolated points are almost the same for both peak I and peak I'.

The reference and measured potentials are indicated in the CV in Fig. 4(c). The vertical lines at the lower (upper) half of the CV indicate that the potentials were set by a negative (positive)-going sweep. The spectrum obtained at $-0.2$ V by the negative-going sweep (black line) exhibits no bands in both the wavenumber regions; hence, the adsorption or desorption of ions and molecules does not occur by this potential step. However, the spectrum obtained at $-0.2$ V by the positive-going sweep (red line) exhibits downward bands at 2908 cm$^{-1}$ and 2820 cm$^{-1}$, together with upward bands at 2925 cm$^{-1}$ and 2850 cm$^{-1}$, respectively. Almost all the same spectral features are observed for potentials that are more negative. The former pair of bands are attributed to the decoupled CH-stretching vibrational mode of the alkyl chain adsorbed on the metallic surface with the flat-on orientation, i.e., the orientation of both the chain axis and the carbon plane are parallel to the surface [7]. The CH bond directed to the surface is weakened by electronic or electrostatic interactions; hence, it exhibits a wavenumber as small as 2820 cm$^{-1}$. In contrast, the CH bond directed to the other side of the surface exhibits almost unperturbed wavenumber, 2908 cm$^{-1}$. These downward bands indicate that the alkyl chains, and hence, the entire DOS molecules, are adsorbed on the Au(111) surface with the flat-on orientation at the reference potential and are detached from the surface at the measured negative potentials. The upward bands are assigned to the anti-symmetric ($\nu_{as}$)- and symmetric ($\nu_{s}$)-stretching vibrational mode of methylenes, or CH$_2$ [31]. The appearance of these bands suggests that the detached alkyl chains drift near the surface with a slightly tilted orientation of the carbon plane, because both $\nu_{as}$ and ($\nu_{s}$) are observed. It should be noted that the transition dipole moment along the surface normal is selectively detected by the IRAS. The bands observed in the SO-stretching vibrational mode region are assigned to the SO$_3$-symmetric stretching mode of the (bi)sulfate anion. The wavenumber of ca. 1225 cm$^{-1}$ at the peaks corresponds to the (bi)sulfate on the Cu-UPD layer [32]. Therefore, these bands indicate the formation of the Cu-UPD layer on the Au(111) electrode.

The charging current $I$ nows. This is caused by the strong interactions between the neutral DOS molecules and the Au(111) surface at the potential of zero charge (pzc), which is estimated at approximately $-0.1$ V [27]. Because the alkyl chains are hydrophobic, they are forced out of the water phase and adsorbed on the Au(111) surface. It is generally accepted that the neutral molecules are preferentially adsorbed on the surface at potentials around the pzc [33–35]. The large adsorption energy of the DOS molecules may surpass the adsorption energy of Cu cations in the random adsorption region, though it is difficult to estimate and compare the adsorption energy at an electrolyzed interface. Owing to the inhibition of copper adsorption, the formation of the $\sqrt{3} \times \sqrt{3}$ structure is delayed until a certain amount of Cu cation is adsorbed on the surface by applying a more negative overpotential. This is why peak I, which corresponds to the formation of the $\sqrt{3} \times \sqrt{3}$ phase, is shifted to a more negative potential for the DOS-modified Au(111) electrode. Ion adsorption is preferred because of the strong electrostatic interactions at sufficiently negative potentials; therefore, the DOS molecules are exchanged with copper and (bi)sulfate ions at a more negative potential and the Cu-UPD layer is formed. Once the Cu-UPD layer is formed, it covers the Au(111) electrode surface in the same potential region as the bare Au(111) electrode, which is suggested by the occurrence of peak I' at almost the same potential as observed for the bare Au(111) electrode. However, the charging current is almost undetectable at potentials more positive than peak I'; hence, the Cu cations and (bi)sulfate anions are com-
pletely removed from the surface and the DOS molecules are re-adsorbed at these potentials. This is in accordance with the IRAS results. It also suggests that the desorbed DOS molecules float near the electrode surface somewhere above the Cu-UPD layer at negative potentials and are ready to be re-adsorbed.

IV. CONCLUSION

The SAM of the DOS molecules affects the Cu-UPD process in the sulfuric acid solution in a different manner depending on the density or chain orientation. The flat-lying SAM of the DOS molecules physisorbed on the Au(111) surface delays the first stage of the Cu-UPD process. In contrast, the SAM of the DOS molecules with the upright standing geometry inhibits the entire Cu-UPD process. The physisorbed DOS molecules are stable at potentials around pzc, which is near the potential of the first stage of the Cu-UPD process, and are not exchanged with ions until sufficient negative potentials are applied.

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